Acta Cryst. (1987). A43, 803–809

Thermal Diffuse Scattering in Time-of-Flight Neutron Diffraction

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(*Received 17 March 1987; accepted 17 June 1987*)

Abstract

The nature of the thermal diffuse scattering (TDS) from long-wavelength acoustic modes of vibration in a single crystal is examined for time-of-flight neutron diffraction. In the neighbourhood of the Bragg reflections there may be gaps or 'windows' in the energy change of the scattered neutrons, in the wavelengths of both incident and scattered radiation, and in the total time of flight. TDS is forbidden within these windows and rises to a steep maximum at the edges: one maximum is due to phonon emission (Stokes process) and the other to phonon absorption (anti-Stokes). The edges of the windows are determined by the sound velocity in the crystal. The sound velocity is readily derived, without employing energy analysis, by measuring the positions of the edges of the time-of-flight window.

1. Introduction

In this paper we shall discuss the nature of the thermal diffuse scattering (TDS) which is observed close to the Bragg reflections in a time-of-flight neutron-diffraction experiment on a single crystal. This problem has already been examined with geometrical arguments linked to the concept of a one-phonon scattering surface (Willis, 1986: hereafter paper I). We shall adopt a more analytical approach, which confirms the results given in paper I and extends these to the more realistic case of elastic anisotropy in the crystal. Our notation is the same as in the glossary of paper I.

There are two measured parameters in a time-of-flight diffraction experiment: total time-of-flight, t, and scattering angle, 2θ. If L_0 and v_0 are the flight path and velocity of the incident neutron, and L and v the corresponding quantities for the scattered neutron, then

$$t = L_0/v_0 + L/v. \tag{1}$$

The wave vectors of the incident and scattered neutrons are

$$\mathbf{k}_0 = k_0\hat{\mathbf{u}}_0 = (m_n v_0/\hbar)\,\hat{\mathbf{u}}_0 \tag{2}$$

and

$$\mathbf{k} = k\hat{\mathbf{u}} = (m_n v/\hbar)\hat{\mathbf{u}}, \tag{3}$$

where m_n is the neutron mass and $\hat{\mathbf{u}}_0$, $\hat{\mathbf{u}}$ are unit vectors whose scalar product is $\cos 2\theta$.

The scattered intensity, then, is measured as a function of time and scattering angle. In the next section we consider the TDS recorded in a detector at a scattering angle which is twice the Bragg angle. The analysis is extended in subsequent sections to detectors offset from the Bragg position.

2. Scattering angle equal to twice the Bragg angle

The angle between the incident beam $\mathbf{k}_0$ and the reciprocal-lattice vector $\mathbf{B}$ is $\pi/2$ plus the Bragg angle θ_B; see Fig. 1. If the detector is set at twice the Bragg angle, it will receive radiation which is Bragg reflected for a wave number k_B of the incident beam given by

$$k_B = |\mathbf{B}|(2\sin\theta_B)^{-1}. \tag{4}$$

The corresponding neutron velocity is

$$v_B = (\hbar/m_n)\,k_B, \tag{5}$$

and because Bragg scattering is elastic [*i.e.* $v_0 = v$ in (1)] the total time of flight is

$$t_B = (L_0 + L)/v_B. \tag{6}$$

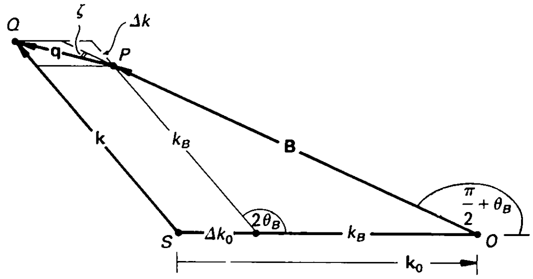

Fig. 1. Vector diagram for scattering to point Q by a phonon of wave vector **PQ**. O is the origin of reciprocal space and P is the reciprocal-lattice point. The scattering angle 2θ is twice the Bragg angle θ_B where $\sin\theta_B = |\mathbf{B}|/2k_B$.

0108-7673/87/060803-07$01.50

Let us turn to inelastic diffuse scattering at the Bragg angle and consider first the restrictions imposed by the conservation of energy and momentum in a one-phonon process. Scattering by creation or annihilation of a phonon of wave vector $\mathbf{q}$ and energy transfer $\hbar\omega(\mathbf{q})$ occurs provided that

$$\mathbf{q} = \Delta k \hat{\mathbf{u}} - \Delta k_0 \hat{\mathbf{u}}_0 \qquad (7)$$

and

$$(\hbar^2/2m_n)(k_0^2 - k^2) = \varepsilon\hbar\omega(\mathbf{q}), \qquad (8)$$

with $\varepsilon = +1$ for creation (neutron energy loss) and $\varepsilon = -1$ for annihilation (energy gain) of a phonon. Δk and Δk_0 in the momentum equation (7) are the quantities defined by

$$\Delta k = k - k_B, \quad \Delta k_0 = k_0 - k_B. \qquad (9)$$

The energy change on the left-hand side of (8) may be expressed, from (5) and (9), as

$$\Delta E = -\hbar(\Delta k - \Delta k_0)[v_B + (\hbar/2m_n)(\Delta k_0 + \Delta k)]. \qquad (10)$$

From Fig. 1 we can see that

$$q \cos \zeta = (\Delta k_0 + \Delta k) \sin \theta_B \qquad (11)$$

and

$$q \sin \zeta = (\Delta k_0 - \Delta k) \cos \theta_B, \qquad (12)$$

where ζ is the angle between the reciprocal-lattice vector and the direction of propagation of the phonon. Thus (8) becomes

$$(\sin \zeta/\cos \theta_B)[v_B + (\cos \zeta)\hbar q/(\sin \theta_B)2m_n] = \varepsilon c_s(\mathbf{q}), \qquad (13)$$

in which $c_s(\mathbf{q})$ $[= \omega(\mathbf{q})/q]$ is the phase velocity of the phonon. If $q = 0$ in (13), it is impossible to satisfy the conditions for one-phonon scattering when

$$(c_s/v_B) \cos \theta_B > 1. \qquad (14)$$

But

$$\sin \theta_B = \lambda/2d = (h/m_n v_B)(1/2d), \qquad (15)$$

so that (14) can be written as

$$d > h/(m_n c_s \sin 2\theta_B) = d_{\min}. \qquad (16)$$

Thus there is no TDS close to the Bragg peak if the spacing exceeds the value of d_{min} *defined in* (16).

Equation (13) can be expressed in terms of the measured time of flight as follows. If Δt represents the difference between the flight time for phonon scattering, t, and the time for Bragg scattering, t_B, we find from (1) and (6) that

$$\Delta t = t - t_B = -(\hbar/m_n v_B^2)(L_0 \Delta k_0 + L \Delta k), \qquad (17)$$

where it is assumed in (17) that Δk_0, Δk are much less than k_B. If Δv_0 and Δv are the differences

$$\Delta v_0 = v_0 - v_B, \qquad \Delta v = v - v_B,$$

(17) can be written

$$\Delta t = -(L_0 \Delta v_0 + L \Delta v)/v_B^2. \qquad (18)$$

We may use the above expressions to express q, Δk_0, Δk in terms of t and ζ, and hence obtain a relation between the time of flight and the direction of those phonons which contribute to the inelastic scattering. From (11) and (12) we have

$$\Delta k_0 \cos(\theta_B + \zeta) = \Delta k \cos(\theta_B - \zeta), \qquad (19)$$

so that (17) can be written

$$\Delta t = -(\hbar \Delta k_0/m_n v_B^2) \times [L_0 + L \cos(\theta_B + \zeta)/\cos(\theta_B - \zeta)]. \qquad (20)$$

From (11) and (13) we obtain

$$(\sin \zeta/\cos \theta_B)[v_B + (\hbar/2m_n)(\Delta k_0 + \Delta k)] = \varepsilon c_s(\mathbf{q})$$

or

$$(\sin \zeta/\cos \theta_B)\{v_B + (\hbar \Delta k_0/2m_n) \times [1 + \cos(\theta_B + \zeta)/\cos(\theta_B - \zeta)]\} = \varepsilon c_s(q), \qquad (21)$$

where we have used (19). Elimination of Δk_0 from (20) and (21) gives

$$\tfrac{1}{2} v_B^2 \Delta t = \left[v_B - \varepsilon \frac{\cos \theta_B}{\sin \zeta} c_s(\mathbf{q})\right] \times \left(\frac{L_0 \cos(\theta_B - \zeta) + L \cos(\theta_B + \zeta)}{\cos(\theta_B - \zeta) + \cos(\theta_B + \zeta)}\right). \qquad (22)$$

Equation (22) is exact provided that $\Delta t \ll t_B$, and this, in turn, implies that we can neglect phonon dispersion and write $c_s(\mathbf{q})$ as a function of ζ only. The equation gives the difference, Δt, between the time of flight for one-phonon TDS and the Bragg time of flight, as the angle of propagation ζ goes from 0 to 2π. If v_B [equal to $(\hbar/2m_n)|\mathbf{B}|/\sin \theta_B$] exceeds $c_s(\zeta) \cos \theta_B$, the TDS covers a continuous range on either side of the Bragg peak at $\Delta t = 0$: we have already seen that, if v_B is less than $c_s(\zeta) \cos \theta_B$, there is a break in the TDS at $\Delta t = 0$.

3. General scattering angle

In the general case the scattering angle 2θ is not equal to $2\theta_B$, and we write

$$\theta = \theta_B + \Delta\theta,$$

where $\Delta\theta$ is the offset angle of the detector from the Bragg setting. New features now appear in the TDS which have no counterpart in the special case of $\Delta\theta = 0$.

Fig. 2 is the diagram for a finite offset which corresponds to Fig. 1 for a zero offset. If we take the real axis of an Argand diagram along the direction of the incident beam, all the vectors in Fig. 2 can be represented by complex numbers:

$$\mathbf{k}_0 \equiv k_B + \Delta k_0$$
$$\mathbf{k} \equiv (k_B + \Delta k)\exp(2i\theta)$$
$$\mathbf{B} \equiv k_B[\exp(2i\theta_B) - 1]$$
$$\mathbf{q} \equiv iq \exp[i(\theta_B + \zeta)].$$

Momentum conservation for one-phonon scattering requires

$$\mathbf{k} - \mathbf{k}_0 = \mathbf{B} - \varepsilon\mathbf{q}$$

or, from the expressions above,

$$\Delta k_0 - \Delta k \exp(2i\theta) = k_B[\exp(2i\theta) - \exp(2i\theta_B)] + i\varepsilon q \exp[i(\theta_B + \zeta)]. \quad (23)$$

Taking real and imaginary parts of (23) gives separate expressions for Δk_0 and Δk,

$$\Delta k_0 \sin 2\theta = -\varepsilon q \cos(2\theta - \theta_B - \zeta) - k_B \sin(2\theta - 2\theta_B) \quad (24)$$

and

$$\Delta k \sin 2\theta = -\varepsilon q \cos(\theta_B + \zeta) - 2k_B \sin(\theta - \theta_B)\cos(\theta + \theta_B). \quad (25)$$

From (8) and (10) the energy-conservation condition may be written

$$(\Delta k_0 - \Delta k)[v_B + (\hbar/2m_n)(\Delta k_0 + \Delta k)] = \varepsilon\omega(\mathbf{q}).$$

For small energy transfers the second term in square brackets may be neglected and this equation reduces to (see paper I)

$$\Delta k_0 - \Delta k = \varepsilon\beta(\zeta)q \quad (26)$$

where $\beta(\zeta)$ is the phase velocity, $c_s(\zeta)$, divided by the neutron velocity, v_B.

We can now establish the conditions for a neutron, scattered through an angle 2θ, to interact with a phonon propagating at an angle ζ to the normal to the reflecting plane. If we substitute (24) and (25) into (26), the magnitude of the phonon wave vector

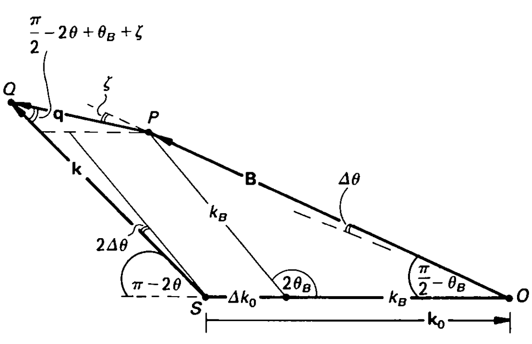

Fig. 2. Vector diagram corresponding to Fig. 1 but with finite offset $\Delta\theta$ from the Bragg position.

will be given by

$$q = \frac{2\varepsilon k_B \sin(\theta - \theta_B)\sin\theta_B}{\sin(\theta - \theta_B - \zeta) - \beta(\zeta)\cos\theta}. \quad (27)$$

Equations (27), (24) and (25) impose restrictions on the ranges of q, Δk_0 and Δk and hence on the time of flight which are possible in one-phonon scattering. In order to discuss the nature of these restrictions, we assume, for the remainder of this section, an isotropic crystal (which, of course, is rarely found in practice), in which β is independent of the direction of propagation ζ. The effects of anisotropy are discussed in § 4. Note also that the neglect of phonon dispersion (β independent of q) limits the discussion to small values of q; the apparent divergence due to the possible vanishing of the denominator in (27) is thus of no consequence.

(*a*) *Allowed energy transfers*

From (10) the energy loss is

$$\Delta E = \hbar(\Delta k_0 - \Delta k)v_B$$

and resubstitution for q in (26) gives the neutron energy loss

$$\Delta E = \frac{4E_B \sin(\theta - \theta_B)\beta\sin\theta_B}{\sin(\theta - \theta_B - \zeta) - \beta\cos\theta} \quad (28)$$

(where E_B is the energy of Bragg-scattered neutrons, $\hbar^2 k_B^2/2m_n$). Thus the range of possible energy transfers, at a given scattering angle 2θ, is determined by the denominator as $\sin(\theta - \theta_B - \zeta)$ varies from -1 to $+1$, or

$$-\pi/2 < \theta - \theta_B - \zeta < \pi/2.$$

Note that we no longer have explicit dependence on the parameter ε, which specifies phonon creation or annihilation; this is now determined by the sign of ΔE, positive for creation and negative for annihilation. There are two cases.

(i) If $\beta\cos\theta > 1$, the denominator in (28) is always less than zero. For $\theta > \theta_B$ only neutron energy gain (phonon annihilation) can occur, while for $\theta < \theta_B$ only energy loss occurs, with energy transfers in the range

$$\frac{\beta\sin\theta_B}{(\beta\cos\theta)+1} < \frac{\Delta E}{4E_B\sin(\theta - \theta_B)} < \frac{\beta\sin\theta_B}{(\beta\cos\theta)-1}. \quad (29)$$

This is the case corresponding to low neutron energy transfer.

(ii) If $\beta\cos\theta < 1$, then for $\theta > \theta_B$ ($\theta < \theta_B$) energy gain (loss) can occur for

$$|\Delta E/4E_B\sin(\theta - \theta_B)| > \frac{\beta\sin\theta_B}{1+\beta\cos\theta} \quad (30)$$

and energy loss (gain) for

$$|\Delta E/4E_B \sin(\theta-\theta_B)| < \frac{\beta \sin\theta_B}{1-\beta\cos\theta}. \quad (31)$$

Thus there is a range of energy transfers

$$-\frac{1}{1+\beta\cos\theta} < \frac{\Delta E}{4E_B\beta\sin\theta_B\sin(\theta-\theta_B)} < \frac{1}{1-\beta\cos\theta}, \quad (32)$$

or a 'window', where no scattering can occur.

This is illustrated for $\theta > \theta_B$ in Fig. 3, where we have plotted the two sides of the energy balance equation (27), written in the form

$$\varepsilon q \sin(\theta-\theta_B-\zeta) - 2k_B\sin(\theta-\theta_B)\sin\theta_B = \varepsilon\beta q\cos\theta. \quad (33)$$

The left-hand side gives a 'fan' of possible neutron energy transfers as ζ is varied (shown by the coarsely hatched area), and the right-hand side gives the phonon energy times cos θ. Three orders of a Bragg reflection are shown, (*a*) corresponding to case (i) and (*b*) and (*c*) to case (ii). The energy windows occur in Figs. 3(*b*) and (*c*) for ΔE lying between the finely hatched lines.

(*b*) *Allowed range of incident and final wave vectors*

A similar argument may be applied to the allowed ranges of Δk_0 and Δk. Substituting for q from (27) into (24) and (25) respectively, one finds, after some algebra,

$$\Delta k_0 \sin\theta = -k_B\sin(\theta-\theta_B) \times\left[\cos\theta_B + \frac{\cos(\theta-\theta_B-\zeta)-\beta\sin\theta}{\sin(\theta-\theta_B-\zeta)-\beta\cos\theta}\sin\theta_B\right] \quad (34)$$

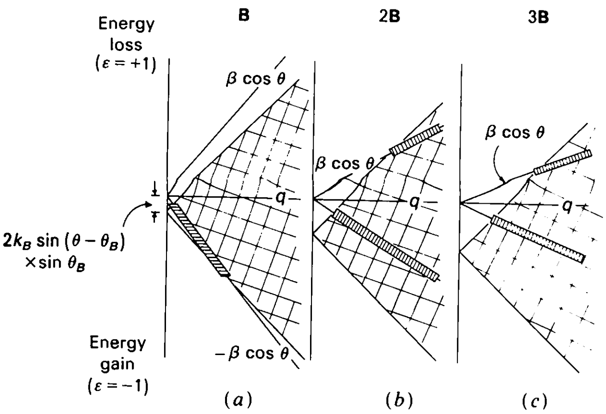

Fig. 3. Diagrams illustrating solution of equation (33) for three successive orders. Note that β cos θ exceeds unity in (*a*) but is less than unity in (*b*) and (*c*).

$$\Delta k \sin\theta = -k_B\sin(\theta-\theta_B) \times\left[\cos\theta_B + \frac{\cos(\theta-\theta_B-\zeta)+\beta\sin\theta}{\sin(\theta-\theta_B-\zeta)-\beta\cos\theta}\sin\theta_B\right]. \quad (35)$$

There will be a gap in the possible incident wavelengths if Δk_0 has maxima and minima as a function of ζ. Differentiation of (34) gives the necessary condition

$$\beta\sin(2\theta-\theta_B-\zeta)=1. \quad (36)$$

This equation has the following interpretation.

Reference to Fig. 2 shows that $(\pi/2-2\theta+\theta_B+\zeta)$ is the angle between the phonon propagation direction $\mathbf{q}$ and the scattered vector $\mathbf{k}$ (angle *PQS*). Equation (36) states that an extremum occurs in Δk_0 when the component of the phonon velocity in the direction of the scattered neutron is equal to the neutron velocity.

Thus unless the neutron velocity is less than the phonon velocity ($\beta > 1$), there is scattering for all values of Δk_0, with no wavelength window - even though there is a finite range of possible energy transfers. However, for $\beta > 1$ there are maximum and minimum values of Δk_0 given by (36) with

$$\cos(2\theta-\theta_B-\zeta)=\pm(1-1/\beta^2)^{1/2}. \quad (37)$$

Substituting for ζ given by (36) and (37) into (34) gives the extreme values of Δk_0 [with the + referring to the positive sign in (37)]:

$$\Delta k_0^{\pm} = k_B(\sin\Delta\theta/\sin\theta) \times\left\{\frac{[\mp(\beta^2-1)^{1/2}+\beta^2\sin\theta\cos\theta]}{(1-\beta^2\cos^2\theta)}\sin\theta_B - \cos\theta_B\right\} \quad (38)$$

where we have now written $\Delta\theta$ for the offset angle $(\theta-\theta_B)$.

Similarly one finds for the scattered wave vector in (35)

$$\Delta k^{\pm} = k_B(\sin\Delta\theta/\sin\theta) \times\left\{\frac{[\mp(\beta^2-1)^{1/2}-\beta^2\sin\theta\cos\theta]}{(1-\beta^2\cos^2\theta)}\sin\theta_B - \cos\theta_B\right\} \quad (39)$$

with the extrema given by

$$\sin(\theta_B+\zeta)=-1/\beta. \quad (40)$$

Returning to Δk_0, equations (34) and (38), we may understand the behaviour in terms of three regions.

(i) $\beta < 1$. This corresponds to case (*a*)(ii), or (*b*) and (*c*) of Fig. 3, where both energy gain and loss can occur. However, the absence of an extremum in Δk_0 indicates that the whole range of Δk_0 can contribute to both branches of the energy transfer. There is therefore no wavelength window.

(ii) $\beta \cos\theta < 1 < \beta$. This also corresponds to case (*a*)(ii), Figs. 3(*b*), (*c*), but now there is an extremum in Δk_0, that is, a limited range of Δk_0 for both phonon creation and annihilation. For $\Delta\theta$ positive, for phonon creation one must have

$$\Delta k_0 > \Delta k_0^+ = \frac{k_B \sin\Delta\theta}{\sin\theta}\left[\frac{(\beta^2-1)^{1/2}\cos\Delta\theta - \sin\Delta\theta}{\sin\theta - (\beta^2-1)^{1/2}\cos\theta}\right], \quad (41)$$

while for phonon annihilation

$$\Delta k_0 < \Delta k_0^- = -\frac{k_B \sin\Delta\theta}{\sin\theta} \times\left[\frac{(\beta^2-1)^{1/2}\cos\Delta\theta + \sin\Delta\theta}{\sin\theta + (\beta^2-1)^{1/2}\cos\theta}\right]; \quad (42)$$

and hence there is a window in Δk_0 of width given by

$$\Delta k_0^+ - \Delta k_0^- = \frac{2k_B \sin\Delta\theta}{\sin\theta}\frac{(\beta^2-1)^{1/2}\sin\theta_B}{(1-\beta^2\cos^2\theta)} \quad (43)$$

and similarly for $\Delta\theta < 0$. Equations (41) and (42) reduce to (36) of paper I for $|\Delta\theta| \ll 1$.

(iii) $\beta\cos\theta > 1$. This corresponds to (*a*)(i) and (*a*) of Fig. 3. Here scattering is only possible over a finite range of Δk_0 lying between $\Delta k_0^\pm$.

This range is given by

$$|\Delta k_0^+ - \Delta k_0^-| = \frac{2k_B |\sin\Delta\theta| (\beta^2-1)^{1/2}\sin\theta_B}{\sin\theta(\beta^2\cos^2\theta - 1)} \quad (44)$$

corresponding to the range of energy transfers in (29). Note, however that the edges of the energy range, given by $\sin(\Delta\theta - \zeta) = \pm 1$, do not correspond to those of the wave vector, as defined by (36). This is because the limits of ΔE are fixed by the maximum and minimum values of $(k^2 - k_0^2)$, whereas the limits of k_0 are determined by the condition that the scattered wave vector just touches the (elliptical) scattering surface (see paper I).

(*c*) *Allowed time of flight*

Finally, for the isotropic case, we consider the allowed ranges of time of flight for one-phonon scattering. The expression for the difference from the Bragg time of flight is given by (17) with (34) and (35).

The first thing to note is that for a diffractometer with a short final flight path, $L \ll L_0$, such as the High Resolution Powder Diffractometer on the ISIS spallation source (Johnson & David, 1985), the difference in time of flight is determined by Δk_0 so that the discussion in (*b*) above applies. However, it is useful to consider the general case. In doing so, we shall initially make the simplification of working only to lowest order in $\Delta\theta$, by neglecting the difference between θ and θ_B in the square brackets in (34) and (35). The full generalization is given in § 4. In this approximation we may write

$$\tau_l(\zeta) = \frac{1}{t_B}\frac{\Delta t(\zeta)}{\Delta\theta} = \cot\theta - \frac{\cos\zeta - (1-2l)\beta\sin\theta}{\sin\zeta + \beta\cos\theta} \quad (45)$$

for the time of flight involving a phonon propagating in the direction ζ, where we have written $l = L/(L_0 + L)$. $\tau_l(\zeta)$ has extrema when

$$\beta[(1-l)\sin(\theta-\zeta) - l\sin(\theta+\zeta)] = 1 \quad (46)$$

[in agreement with (36) and (40), for $l = 0, 1$]. Solutions to this equation exist provided

$$\beta^2[\cos^2\theta + (1-2l)^2\sin^2\theta] > 1, \quad (47)$$

which is equivalent to

$$(1/v_B)(L_0^2 + L^2 + 2L_0L\cos 2\theta)^{1/2} > (1/c_s)(L_0 + L).$$

Equation (47) thus replaces $\beta > 1$ as the condition for a time-of-flight window to exist for general l. This condition has a very strange interpretation: in order to obtain an 'edge' in the spectrum it is necessary that the time taken for the neutron to travel in a direct line from the source to the detector be longer than would be required for the phonon to travel from the source to the sample position and from there to the detector!

The optimum condition for observing edges to the scattering is therefore that one or other of the flight paths should be as short as possible.

Fig. 4 illustrates the possible time-of-flight values. If we write (45), in an analogous fashion to (33), as

$$\cos\zeta + (\tau - \cot\theta)\sin\zeta = \beta[(1-2l)\sin\theta - (\tau - \cot\theta)\cos\theta] \quad (48)$$

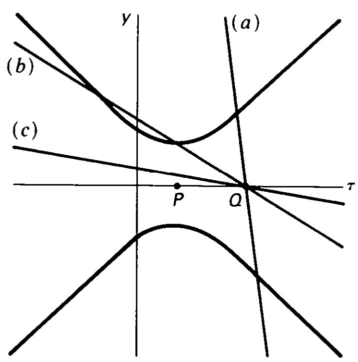

Fig. 4. Diagram illustrating solutions of equation (48). $\beta\cos\theta$ exceeds unity in (*a*); (*b*) and (*c*) correspond to $\beta\cos\theta < 1$ and $A\beta \lessgtr 1$, where $A^2 = (L_0^2 + L^2 + 2L_0L\cos 2\theta)/(L_0 + L)^2$. The point P corresponds to $\tau = \cot\theta$ and $PQ = (1-2l)\tan\theta$; the lines have slopes $-\beta\cos\theta$.

then we see that as ζ varies from 0 to 2π, the left-hand side, for a given τ, lies between the values $\pm[1+(\tau-\cot\theta)^2]^{1/2}$. In other words, the values of the left-hand side for which scattering is possible lie between the two sheets of the rectangular hyberbola

$$y^2=1+(\tau-\cot\theta)^2. \quad (49)$$

Edges occur where y is equal to the right-hand side of (48). Thus if $\beta\cos\theta>1$ [Fig. 4, line (a)] there is a band of scattering. If $\beta\cos\theta<1$ there is a window or not [Fig. 4, lines (b) and (c) respectively] according to whether the line cuts the hyperbola. This condition is given by (47). Note that if $l=\frac{1}{2}$ (equal flight paths), no window can occur. The phonon velocity is given in terms of the positions of the edges by

$$\beta=\frac{[1+(\tau-\cot\theta)^2]^{1/2}}{|(1-2l)\sin\theta-(\tau-\cot\theta)\cos\theta|}. \quad (50)$$

When (46) is satisfied, the extreme time-of-flight values are given by

$$\tau_l^{\pm}=\cot\theta-\frac{\beta^2(1-2l)\cos\theta\sin\theta\pm(A^2\beta^2-1)^{1/2}}{1-\beta^2\cos^2\theta}, \quad (51)$$

where $A^2\beta^2$ is the left-hand side of (47). Thus A is the ratio of the direct distance from source to detector divided by the sum of the path lengths. Following the discussion of (b) above, we find that the width of the time-of-flight window ($\beta\cos\theta<1$) or the width of the time-of-flight spectrum ($\beta\cos\theta>1$) is given by

$$|t^+-t^-|=2t_B|\Delta\theta|(A^2\beta^2-1)^{1/2}\,|1-\beta^2\cos^2\theta|. \quad (52)$$

Note that l enters this expression only in the term A in the numerator.

The time of flight at the centroid of the window is given by

$$\tfrac{1}{2}(t^++t^-)-t_B=-t_B\Delta\theta[\beta^2(1-2l\sin\theta)-1](\cot\theta)\times(1-\beta^2\cos^2\theta)^{-1}. \quad (53)$$

4. Crystal anisotropy

In the preceding section we have examined the theory of the one-phonon diffraction by elastically isotropic crystals. This restriction was made in order to seek insight into the nature of the 'edges' and 'windows' which occur in the scattering. However, if the theory is to be applied in a quantitative manner to real crystals, then it is necessary to examine the anisotropic case, in which one no longer assumes that $\beta(\zeta)$, the ratio of phonon phase velocity to neutron velocity is independent of propagation direction.

In the following we also remove the restriction of small $\Delta\theta$. However, we retain the approximations involved in (17) and (26). In this generalization, (45) becomes

$$\tau(\zeta)=(1/t_B[\Delta t(\zeta)/\sin\Delta\theta]=\frac{1}{\sin\theta}\left[\cos\theta_B-\frac{\cos(\zeta-\Delta\theta)-(1-2l)\beta(\zeta)\sin\theta}{\sin(\zeta-\Delta\theta)+\beta(\zeta)\cos\theta}\sin\theta_B\right], \quad (54)$$

which may be written analogously to (48) as

$$\beta^{-1}(\zeta)[\sin\theta_B\cos(\zeta-\Delta\theta)+T\sin(\zeta-\Delta\theta)]=(1-2l)\sin\theta_B\sin\theta-T\cos\theta \quad (55)$$

with

$$T=\tau\sin\theta-\cos\theta_B. \quad (56)$$

For a given τ, the upper and lower bounds on the left-hand side are now given by

$$[\sin\theta_B\sin(\zeta-\Delta\theta)-T\cos(\zeta-\Delta\theta)]\beta(\zeta)+[\sin\theta_B\cos(\zeta-\Delta\theta)+T\sin(\zeta-\Delta\theta)]\beta'(\zeta)=0, \quad (57)$$

where the prime indicates differentiation with respect to ζ.

Now the phonon frequency is given by

$$\omega(\mathbf{q})=c(\zeta)q,$$

so that the group velocity of the phonon, given by the gradient of $\omega(\mathbf{q})$, has components $c(\zeta)$ along the direction of $\mathbf{q}$ and $c'(\zeta)$ perpendicular to this direction. Hence, if α is the angle between the direction of group propagation and the phonon wave vector, then

$$\cos\alpha=\beta(\zeta)/\beta_g(\zeta) \text{ and } \sin\alpha=\beta'(\zeta)/\beta_g(\zeta), \quad (58)$$

where β_g is the magnitude of the group velocity divided by the neutron velocity:

$$\beta_g^2(\zeta)=\beta^2(\zeta)+\beta'^2(\zeta). \quad (59)$$

With this substitution, (57) yields

$$\tan(\zeta+\alpha-\Delta\theta)=T/\sin\theta_B \quad (60)$$

and it follows that the left-hand side of (55) is bounded by the values

$$Y=\pm\beta_g^{-1}[\sin^2\theta_B+T^2]^{1/2}. \quad (61)$$

Here β_g is the group velocity of a phonon whose direction of (group) propagation relative to the Bragg direction is given by

$$\zeta+\alpha=\theta-\theta_B+\tan^{-1}(T/\sin\theta_B). \quad (62)$$

Thus, if an edge in the time-of-flight spectrum is observed at a particular value of τ [or time of flight Δt, given by (54)], then it corresponds to the creation or annihilation of a phonon group of velocity

$$\beta_g = \frac{[1-2\tau \sin\theta \cos\theta_B + \tau^2 \sin^2\theta]^{1/2}}{|(1-2l)\sin\theta_B \sin\theta + \cos\theta_B \cos\theta - \tau \sin\theta \cos\theta|} \quad (63)$$

[which reduces to (50) as $\theta \to \theta_B$].

Conversely, the edges of the time-of-flight spectrum are given by

$$\tau^{\pm} = \frac{1}{\sin\theta}\left[\cos\theta_B - \frac{(1-2l)\sin\theta\cos\theta\,\beta_{\pm}^2 \pm (A^2B_{\pm}^2-1)^{1/2}}{1-\beta_{\pm}^2\cos^2\theta}\sin\theta_B\right] \quad (64)$$

as the generalization of (51). In the anisotropic case the two edges of the window correspond in general to different phonon propagation directions, with different group velocities, denoted here by $\beta_{\pm}$.

This difference may be illustrated by the special case $l=0$, $\Delta\theta$ small. Then, the condition for extrema in $\tau(\zeta)$, equation (54), becomes

$$\sin(\theta-\zeta-\alpha) = \beta_g^{-1}(\zeta). \quad (65)$$

Were β_g independent of ζ, this would have solutions

$$\zeta+\alpha = \theta - \sin^{-1}\beta_g^{-1}$$
$$\zeta+\alpha = \pi+\theta+\sin^{-1}\beta_g^{-1}.$$

But these only represent equivalent directions in the crystal if $\theta=0$ or $\pi/2$ and only then if the crystal is centrosymmetric. Therefore, in general, the two solutions of (65) (with positive and negative cosine) have different solutions both for ζ and for β. In the case of crystal anisotropy, one may determine two values of the group velocity at two propagation directions from the edges of the window [determined by (63) and (62)], but one may not use the width of the window.

5. Concluding remarks

In a one-phonon neutron scattering experiment employing time-of-flight Laue diffraction, gaps or 'windows' appear in (i) the energy change of the neutrons, (ii) the incident and scattered wavelengths, and (iii) the total time of flight. We have discussed the conditions for these windows to appear and shown that, in each case, the edges of the window are determined by the sound velocity in the crystal. In the absence of energy analysis, the velocity is obtained most readily from the edges of the time-of-flight window. The theory, which is restricted to acoustic modes of long wavelength, has been given for both isotropic and anisotropic propagation of sound.

For the isotropic case we have reproduced the results of Willis (1986). The main result of this paper has been to generalize the theory to the case of elastic anisotropy. The principal effect has been to replace the phonon phase velocity by the group velocity in expressions determining the positions of edges of regions where one-phonon scattering is possible in time-of-flight diffraction. These edges correspond to phonons whose group velocity and propagation direction are determined by the time of flight [(63) and (62)]. If $\beta_g \cos\theta > 1$, the edges bound regions of scattering; if $\beta_g \cos\theta < 1$, then the edges bound windows where no one-phonon scattering is possible, provided that β_g is sufficiently large [greater than unity for a spectrometer with one flight path much longer than the other or, more generally, as given by (47)]. If β_g is less than this value, the scattering is continuous.

Work described in this paper was undertaken as part of the Underlying Research Programme of the UKAEA. The authors benefited from numerous discussions with Dr C. J. Carlile of the Rutherford Appleton Laboratory and with Dr C. G. Windsor of the Harwell Laboratory.

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